

COSMETIC FORMULATIONS COMPRISING DIKETO DIPHENYL PYRROLO-PYRROLE PIGMENTS

The present invention relates to cosmetic formulations comprising at least one pigment with an intense and saturated colour, more especially, to compositions for making up the skin, both of the face and of the human body, keratinous fibers or superficial body growths, such as the nails, eyelashes, eyebrows or hair, and the lips.

Makeup compositions, such as free or compacted powders, foundations, face powders, eyeshadows, lipsticks, products for concealing rings under the eyes, blushers, mascaras, eyeliners, lip pencils, eyeliner pencils, nail varnishes and products for making up the body are composed of an appropriate vehicle and of colouring agents of different natures intended to confer a certain colour on these compositions before and/or after their application to the skin, lips and/or superficial body growths.

These colouring agents can be lakes, inorganic or organic pigments and/or pearlescent pigments or alternatively colorants. Cosmetic scientists have available pigments of inorganic origin, such as iron oxides or mixtures of brown-yellow iron oxides, and pigments of organic origin. Inorganic pigments, in particular inorganic oxides, have the advantage of being very stable but have the disadvantage of giving rather drab and pale colours. Organic lakes have the advantage of conferring more saturated colours on the compositions but the majority is unstable with respect to light, temperature or pH. Some of these lakes also exhibit the disadvantage of staining the skin in an unsightly way after application, by escape of the colorant. Pearlescent pigments, for their part, make it possible to obtain varied but never intense colours with effects which are iridescent but which are generally fairly weak.

Therefore, there is still a need for further formulations having improved colour strength and saturated shades which, in addition to good tolerability, additionally exhibit outstanding fastness properties in as many areas as possible.

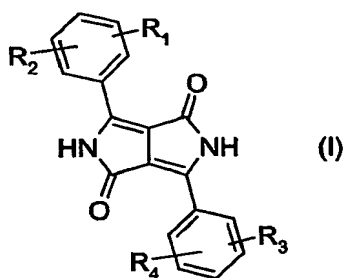
It has now been found that the formulations according to the invention meet those requirements.

By virtue of the pigments used according to the invention in the novel formulations, it is possible to obtain colour shades that hitherto were difficult to achieve or could not be

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achieved at all. The new pigment formulations have outstanding pigmentary properties, such as lightfastness, chroma/saturation, colour strength, hiding power and dispersibility. Further, the colour is almost identical with the colour that can be achieved on the skin and nails using the novel formulations. As a result it is very readily possible to achieve precisely the desired colour shade. The novel formulations are distinguished especially by the fact that they exhibit no "bleeding" of the pigments into the skin and the nails, that is to say sharp outlines are obtained therewith on the skin and the nails themselves are not stained.

An embodiment of the invention is a cosmetic formulation comprising at least one pigment of formula (I)

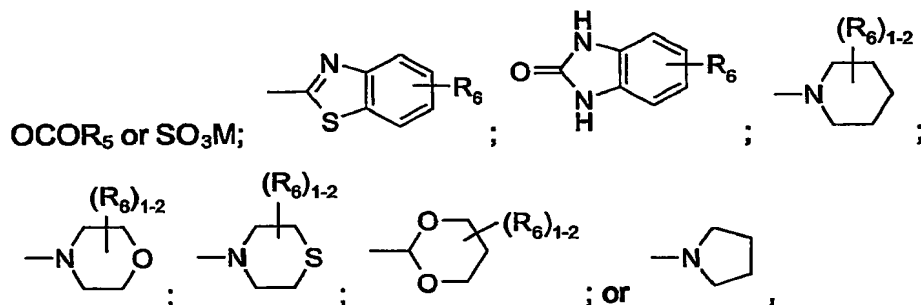


wherein

R_1 , R_2 , R_3 and R_4 independently from each other signify hydrogen; cyano; halogen; CF_3 ; NH_2 ; NR_5R_6 ; NR_5COR_6 ; $COOR_6$; $CONH_2$; $CONR_5R_6$; OR_6 ; $OCOR_6$; SR_5 ; SOR_5 ; SO_2R_5 ; $SO_2NR_5R_6$; SO_2OR_5 ; CHO ; $Si(R_5)_3$; SO_3M ; linear or branched C_1 - C_{30} alkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or branched C_0 - C_{30} alkylene- C_3 - C_{12} cycloalkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or branched C_3 - C_{30} alkenylene- C_3 - C_{12} cycloalkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or branched C_3 - C_{30} alkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or branched C_0 - C_{30} alkylene- C_3 - C_{12} cycloalkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or branched C_3 - C_{30} alkenylene- C_3 - C_{12} cycloalkenyl, which can be unsubstituted or substituted by one or more halogen, OH,

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OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; phenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₁-C₆alkoxy, halogen, cyano or formyl; linear or branched C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆,



wherein

R₅ signifies linear or branched C₁-C₃₀alkyl; C₃-C₃₀-alkenyl; C₃-C₁₂cycloalkyl; C₆-C₁₄aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen; C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen or C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen,

R₆ signifies hydrogen; linear or branched C₁-C₃₀alkyl; C₃-C₃₀-alkenyl; C₃-C₁₂cycloalkyl; C₆-C₁₄aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen; C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen or C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen, and

M signifies hydrogen; a metal; or an unsubstituted or substituted ammonium group,

wherein the pigments have a specific surface area (BET) of 6 – 200 m²/g, and with the proviso that

(i) if R₁ is H, then R₂ is not H, C₁-C₁₈alkyl, C₁-C₄alkoxy, halogen, phenyl or SO₃M.

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Preferably, the pigments have a specific surface area (BET) of 8 – 170 m²/g, even more preferred of 10 – 150 m²/g.

The specific surface area (BET) is measured according to the method developed by
 5 Brunauer, Emmet and Teller. The standardized method is described in DIN 66131 and DIN 66132.

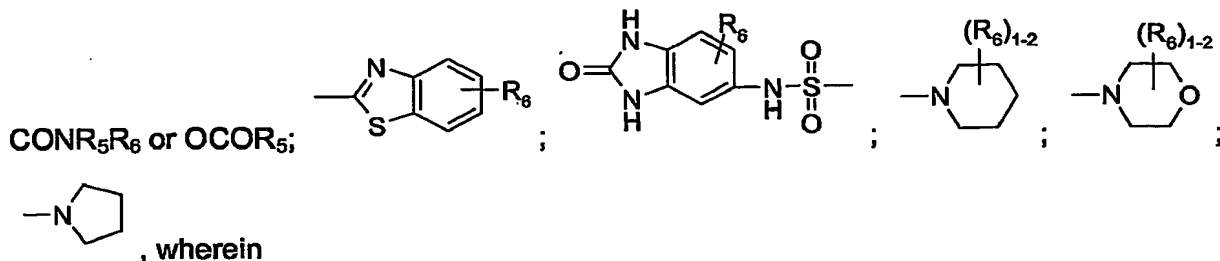
The alkyl and alkoxy radicals can be linear or branched and can be chosen for example, from
 methyl, ethyl, n- and isopropyl, n-, sec-, tert- or isobutyl, n-, sec-, tert- or isopentyl radicals;
 10 the alkenyl radicals can be linear or branched and can be chosen for example from allyl,
 methallyl, 2-butenyl, 2-hexenyl, 3-hexenyl or 2-octenyl radicals.
 The alkyl chains can also interrupted by one or more heteroatoms, such as N, O or S.

The halogen atom can preferably be Cl, Br or F.
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M can be hydrogen, sodium, potassium, lithium or an ammonium group.

In a preferred embodiment of the present invention R₁, R₂, R₃ and R₄ signify independently
 from each other hydrogen; cyano; halogen; CF₃; SR₅; SOR₅; SO₂R₅; SO₂NR₅R₆; NR₅R₆;
 20 COOR₆; CONH₂; CONR₅R₆; OCOR₅; linear or branched C₁-C₁₈alkyl, which can be
 unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; linear or branched
 C₀-C₂₄alkyleneC₃-C₈cycloalkyl, which can be unsubstituted or substituted by one or more
 OR₅, SR₅, NR₅R₆ or COOR₆; linear or branched C₃-C₂₄alkenyleneC₃-C₈cycloalkyl, which can
 be unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; linear or
 25 branched C₃-C₂₄alkenyl, which can be unsubstituted or substituted by one or more OR₅, SR₅,
 NR₅R₆ or COOR₆; linear or branched C₀-C₂₄alkyleneC₃-C₈cycloalkenyl, which can be
 unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; linear or branched
 C₃-C₂₄alkenylene-C₃-C₈cycloalkenyl, which can be unsubstituted or substituted by one or
 more OR₅, SR₅, NR₅R₆ or COOR₆; phenyl, which can be unsubstituted or substituted by one
 30 or more methyl, methoxy or cyano; linear or branched C₁-C₁₈alkoxy, which can be
 unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆,

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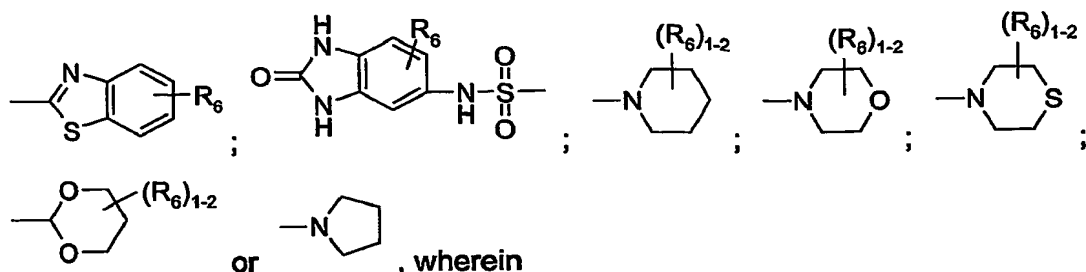


R_5 and R_6 have the meaning as defined above, preferably

- R_5 signifies linear or branched $\text{C}_1\text{-C}_{18}$ alkyl; $\text{C}_3\text{-C}_{18}$ alkenyl; $\text{C}_3\text{-C}_8$ cycloalkyl; $\text{C}_6\text{-C}_{10}$ aryl, which
 5 can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl or $\text{C}_1\text{-C}_6$ alkoxy; $\text{C}_7\text{-C}_8$ aralkyl, which can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl or $\text{C}_1\text{-C}_6$ alkoxy; or $\text{C}_8\text{-C}_{12}$ aralkenyl, which can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl or $\text{C}_1\text{-C}_6$ alkoxy and preferably
 R_6 signifies hydrogen; linear or branched $\text{C}_1\text{-C}_{18}$ alkyl; $\text{C}_3\text{-C}_{18}$ alkenyl; $\text{C}_3\text{-C}_8$ cycloalkyl; $\text{C}_6\text{-C}_{10}$ aryl, which can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl
 10 or $\text{C}_1\text{-C}_6$ alkoxy; $\text{C}_7\text{-C}_8$ aralkyl, which can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl or $\text{C}_1\text{-C}_6$ alkoxy; or $\text{C}_8\text{-C}_{12}$ aralkenyl, which can be unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_5\text{-C}_6$ cycloalkyl or $\text{C}_1\text{-C}_6$ alkoxy, wherein the pigments have a specific surface area (BET) of 6 – 200 m^2/g , and
 15 with the proviso that
 (i) if R_1 is H, then R_2 is not H, $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, halogen or phenyl.

- In an especially preferred embodiment of the present invention R_1 , R_2 , R_3 and R_4 independently from each other signify hydrogen; cyano; CF_3 ; SR_5 ; $\text{SO}_2\text{NR}_5\text{R}_6$; NR_5R_6 ;
 20 COOR_6 ; CONH_2 ; CONR_5R_6 ; OCOR_5 ; Cl; F; Br; linear or branched $\text{C}_1\text{-C}_{18}$ alkyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ; linear or branched $\text{C}_0\text{-C}_6$ alkylene $\text{C}_3\text{-C}_8$ cycloalkyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ; linear or branched $\text{C}_3\text{-C}_6$ alkenylene $\text{C}_3\text{-C}_8$ cycloalkyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ;
 25 $\text{C}_3\text{-C}_6$ alkenyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ; linear or branched $\text{C}_0\text{-C}_6$ alkylene $\text{C}_3\text{-C}_8$ cycloalkenyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ; linear or branched $\text{C}_3\text{-C}_6$ alkenylene $\text{C}_3\text{-C}_8$ cycloalkenyl, which can be unsubstituted or substituted by one or more OR_5 , SR_5 , NR_5R_6 or COOR_6 ; phenyl, which can be unsubstituted or substituted by one or more methyl,
 30 methoxy or cyano; linear or branched $\text{C}_1\text{-C}_6$ alkoxy, which can be unsubstituted or substituted by one or more halogen, OH, OR_5 , SR_5 , NH_2 , NR_5R_6 , COOR_6 , CONR_5R_6 , OCOR_5 ;

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R_5 signifies linear or branched C_1 - C_{18} alkyl; C_3 - C_6 alkenyl; C_3 - C_8 cycloalkyl; C_6 - C_{10} aryl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 -

5 C_6 alkoxy; C_7 - C_8 aralkyl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 - C_6 alkoxy; or C_8 - C_{12} aralkenyl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 - C_6 alkoxy,

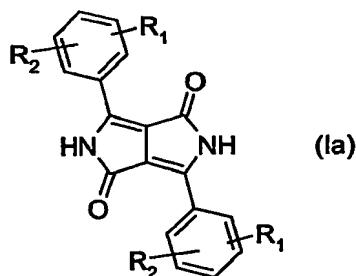
R_6 signifies hydrogen; linear or branched C_1 - C_6 alkyl; C_3 - C_6 alkenyl; C_3 - C_8 cycloalkyl; C_6 -

10 C_{10} aryl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 - C_6 alkoxy; C_7 - C_8 aralkyl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 - C_6 alkoxy; or C_8 - C_{12} aralkenyl, which can be unsubstituted or substituted by one or more C_1 - C_6 alkyl, C_5 - C_6 cycloalkyl or C_1 - C_6 alkoxy,

wherein the pigments have a specific surface area (BET) of 8 – 170m²/g, and with the proviso that

15 (i) if R_1 is H, then R_2 is not H, C_1 - C_{18} alkyl, C_1 - C_4 alkoxy, Cl, F, Br or phenyl.

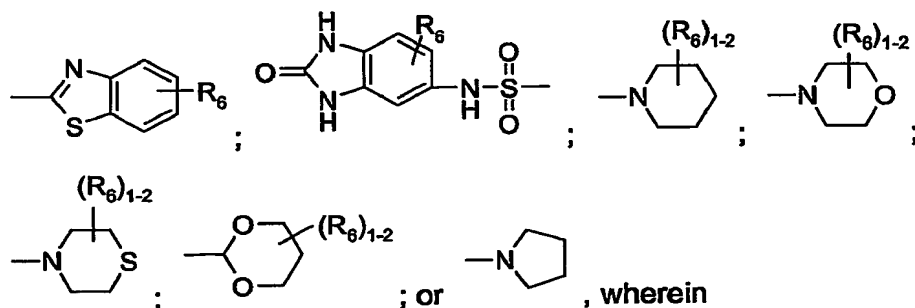
An important embodiment of the invention is a cosmetic formulation comprising at least one pigment of formula (Ia)



20 wherein

R_1 and R_2 independently from each other signify hydrogen; cyano; halogen; CF_3 ; NH_2 ; NR_5R_6 ; NR_5COR_5 ; $COOR_6$; $CONH_2$; $CONR_5R_6$; OR_6 ; $OCOR_5$; SR_5 ; SOR_5 ; SO_2R_5 ; $SO_2NR_5R_6$; SO_2OR_5 ; CHO ; $Si(R_5)_3$; SO_3M ; linear or branched C_1 - C_{30} alkyl, which can be unsubstituted or substituted by one or more halogen, 25 OH , OR_5 , SR_5 , NH_2 , NR_5R_6 , $COOR_6$, $CONR_5R_6$, $OCOR_5$ or SO_3M ; linear or

branched C₀-C₃₀alkyleneC₃-C₁₂cycloalkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₃-C₃₀alkenylene-C₃-C₁₂cycloalkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₃-C₃₀alkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₀-C₃₀alkyleneC₃-C₁₂cycloalkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₃-C₃₀alkenylene-C₃-C₁₂cycloalkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; phenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₁-C₆alkoxy, halogen, cyano or formyl; linear or branched C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M; linear or branched C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆, OCOR₅ or SO₃M;



R₅ signifies linear or branched C₁-C₃₀alkyl; C₃-C₃₀-alkenyl; C₃-C₁₂cycloalkyl; C₆-C₁₄aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen; C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen or C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen,

R₆ signifies hydrogen; linear or branched C₁-C₃₀alkyl; C₃-C₃₀-alkenyl; C₃-C₁₂cycloalkyl; C₆-C₁₄aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen;

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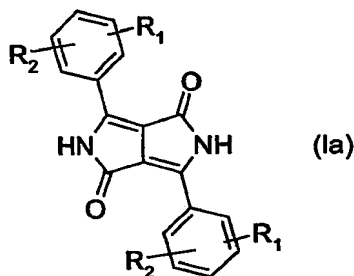
C₇-C₂₄aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen or C₈-C₂₄aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl, C₁-C₆alkoxy, C₁-C₆thioalkyl or halogen, and

5 M signifies hydrogen; a metal atom or an ammonium group, wherein the pigments have a specific surface area (BET) of 10 – 150 m²/g, and with the proviso that

(i) if R₁ is H, then R₂ is not H, C₁-C₁₈alkyl, C₁-C₄alkoxy, halogen, phenyl or SO₃M.

10 All preferences of R₁ and R₂ as defined for the compounds of formula (I) do also apply for the compounds of formula (Ia).

A very important embodiment of the invention is a cosmetic formulation comprising at least one pigment of formula (Ia)



15 wherein

R₁ and R₂ independently from each other signify hydrogen; cyano; CF₃; SR₅; SO₂NR₅R₆;

NR₅R₆; COOR₆; CONH₂; CONR₅R₆; OCOR₅; Cl; F; Br; linear or branched C₁-C₁₈alkyl, which can be unsubstituted or substituted by one or more OR₅, SR₅,

20 NR₅R₆ or COOR₆; linear or branched C₀-C₆alkyleneC₃-C₈cycloalkyl, which can be unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; linear or branched C₃-C₆alkenyleneC₃-C₈cycloalkyl, which can be unsubstituted or

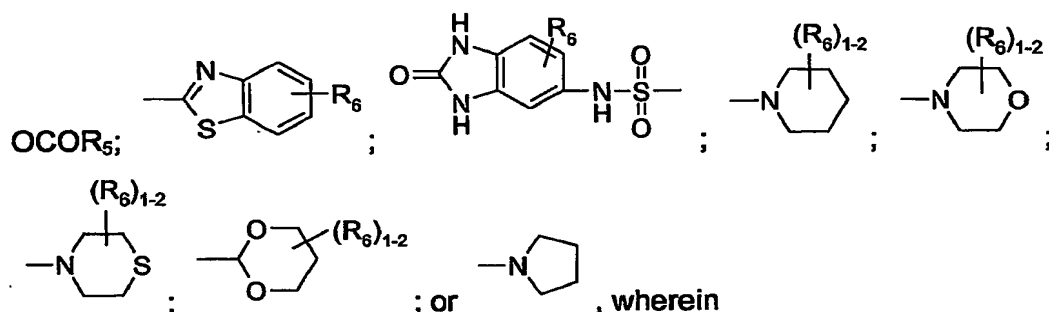
substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; linear or branched C₃-C₆alkenyl, which can be unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆;

25 NR₅R₆ or COOR₆; linear or branched C₀-C₆alkyleneC₃-C₈cycloalkenyl, which can be unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆;

linear or branched C₃-C₆alkenylene-C₃-C₈cycloalkenyl, which can be

unsubstituted or substituted by one or more OR₅, SR₅, NR₅R₆ or COOR₆; phenyl, which can be unsubstituted or substituted by one or more methyl, methoxy or

cyano; linear or branched C₁-C₆alkoxy, which can be unsubstituted or substituted by one or more halogen, OH, OR₅, SR₅, NH₂, NR₅R₆, COOR₆, CONR₅R₆,



- 5 R₅ signifies linear or branched C₁-C₆alkyl; C₃-C₆alkenyl; C₃-C₈cycloalkyl; C₆-C₁₀aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy; C₇-C₈aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy; or C₈-C₁₂aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy,
- 10 R₆ signifies hydrogen; linear or branched C₁-C₆alkyl; C₃-C₆alkenyl; C₃-C₈cycloalkyl; C₆-C₁₀aryl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy; C₇-C₈aralkyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy; or C₈-C₁₂aralkenyl, which can be unsubstituted or substituted by one or more C₁-C₆alkyl, C₅-C₆cycloalkyl or C₁-C₆alkoxy,
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wherein the pigments have a specific surface area (BET) of 6 – 200 m²/g, preferably 8 – 170 m²/g, more preferably 10 – 150 m²/g, and with the proviso that

- (i) if R₁ is H, then R₂ is not H, C₁-C₁₈alkyl, C₁-C₄alkoxy, Cl, F, Br or phenyl.

20 The pigment of the invention may be transparent or opaque and can be a physical mixture or a solid solution or a mixed crystal of two or more pigments of the formula (I) or of pigments of the formula (I) with one or more of other organic pigments. The pigment of the invention may optionally be combined with other pigments for shifting the colour of the formulation or for enhancing the colour power and/or goniochromatic properties of crystal liquid or multilayer pigments having goniochromatic properties.

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30 The manufacture of the diketodiarylpyrrolo-pyrroles of formula (I) is disclosed in particular in the Ciba-Geigy documents EP-A-94,911, EP-A-542,669, EP-A-787,730, EP-A-787,731 and WO-A-96/08537. The specific surface area (BET) and the average primary particle size can

be controlled by commonly known methods, such as growth inhibitors, acid pasting, basic reprecipitation, mechanical methods, for example dry (salt) grinding (or milling), kneading, wet milling etc.

- 5 The pigment according to the invention may be incorporated in a cosmetic formulation, in an amount which can be easily determined by a person skilled in the art on the basis of his broad knowledge and which can in particular range from 0.01 to 50% by weight with respect to the weight of the formulation, preferably in an amount ranging from 0.5 to 25% by weight. This pigment can be also fixed on a polymer in particular by graphing or embedding.
- 10 Moreover, it is also possible to use one or more pigments of formula (I) together with other pigments, goniochromatic pigments and/or colourants such as are employed in cosmetic formulations. Pigments other than those of formula (I) may be present in the formulation in an amount ranging from 0 to 25% of the weight of the final formulation and preferably from 2 to 15%. Preferred inorganic pigments are, for example, titanium, zirconium or cerium oxides, as
- 15 well as zinc, iron or chromium oxides and ferric blue. Preferred organic pigments are, for example, carbon black and barium, strontium, calcium and aluminium lakes.
- Further suitable pigments are those described in EP408498, EP953343 or WO0033795.

- If desired, the pigments may also be used in the form of surface-modified pigments, for
- 20 example modified by perfluoroalkyl phosphate, methylpolysiloxanes, methyl-hydrogen-poly-siloxanes or chitosan. Suitable modified pigments are, for example, those described by B. G. Hays in Am. Inkmaker, (June, 1984) 28, (Oct., 1986) 13 and (Nov., 1990) 28.

- In addition, it is also possible to use solid solutions of the pyrrolo-[3,4-c]-pyrroles, for example
- 25 solid solutions consisting of two different compounds of that type, such as are described in US Patent Specification 4 783 540, or solid solutions of pyrrolo-[3,4-c]-pyrroles and quinacridones, such as are described in US Patent Specification 4 810 304, or solid solutions consisting of two different pyrrolo-[3,4-c]-pyrroles and quinacridones, such as are described in US Patent Specification 5 529 623.

- 30 Such optionally modified pigments are advantageously used in the form of pigment preparations in which the pigment is already in dispersed form. Suitable preparations are described, for example, in W. Herbst, K. Hunger: Industrielle organische Pigmente, VCH Verlagsgesellschaft 1995, page 92 ff.

Therefore, a further embodiment of the present invention relates to a cosmetical formulation comprising, based on the total weight of the formulation,

- a) from 0.0001 to 50 % by weight, preferably from 0.0001 to 25 % by weight, of at least one pigment of formula (I), and
- 5 b) from 50 to 99.9999 % by weight, preferably from 75 to 99.9999 % by weight, of a cosmetically suitable carrier.

The pigments according to the present invention can have a broad range of primary particle size. The average primary particle size of the pigments depends on their use. The primary
10 particle size is defined as the length of the longest dimension and it is estimated by the analysis of the transmission electron microscopy.

The pigments according to the present invention used in cosmetic preparations and formulations have preferably an average primary particle size of 0.1 – 1µm. For certain uses the average primary size of the pigments can be up to 2.0µm. For other uses, the average
15 primary size of the pigments can be even smaller than 0.1µm. More preferably the average primary size of the pigments according to the present invention have an average primary particle size < 0.2µm and > 0.01µm, preferably > 0.015 µm, even more preferably >0.02µm. Especially preferably, the pigments according to the present invention have an average primary particle size < 0.1µm and > 0.01µm, preferably > 0.015 µm, even more preferably
20 >0.02µm.

Suitable carriers for the cosmetic preparations and formulations according to the invention are the conventional materials used in such compositions.

25 The cosmetic preparations and formulations according to the invention may be in the form of, for example, sticks, ointments, creams, emulsions, suspensions, dispersions, powders or solutions. They are, for example, lipsticks, mascara preparations, make-up for the cheeks, eyeshadows, foundations, eyeliners, powders or nail varnishes.

30 When the preparations are in the form of sticks, for example lipsticks, eyeshadows, make-up for the cheeks or foundations, such preparations consist for a considerable part of fatty components, which may consist of one or more waxes, for example ozocerite, lanolin, lanolin alcohol, hydrogenated lanolin, acetylated lanolin, lanolin wax, beeswax, candelilla wax, microcrystalline wax, carnauba wax, cetyl alcohol, stearyl alcohol, cocoa butter, lanolin fatty

acids, petrolatum, petroleum jelly, mono-, di- or tri-glycerides or -fatty esters that are solid at 25°C, silicone waxes, such as methyloctadecane-oxypolysiloxane and poly(dimethylsiloxy)-stearoxysiloxane, stearic acid monoethanolamine, colophane and derivatives thereof, such as glycol abietates and glycerol abietates, hydrogenated oils that are solid at 25°C, sugar
5 glycerides and oleates, myristates, lanolates, stearates and dihydroxy stearates of calcium, magnesium, zirconium and aluminium.

The fatty component may also consist of a mixture of at least one wax and at least one oil, in which case the following oils, for example, come into consideration: paraffin oil, purcellin oil,
10 perhydrosqualene, sweet almond oil, avocado oil, calophyllum oil, castor oil, sesame oil, jojoba oil, mineral oils having a boiling point of approximately from 310 to 410°C, silicone oils, such as dimethylpolysiloxane, linoleic alcohol, linolenic alcohol, oleyl alcohol, cereal grain oils, such as wheatgerm oil, isopropyl lanolate, isopropyl palmitate, isopropyl myristate, butyl myristate, cetyl myristate, hexadecyl stearate, butyl stearate, decyl oleate, acetyl glycerides,
15 octanoates and decanoates of alcohols and polyalcohols, for example of glycol and glycerol, ricinoleates of alcohols and polyalcohols, for example of cetyl alcohol, isostearyl alcohol, isocetyl lanolate, isopropyl adipate, hexyl laurate and octyldodecanol.

The fatty components in such preparations in the form of sticks may generally account for up to 99.9999 % by weight of the total weight of the preparation.

20 The cosmetic preparations and formulations according to the invention may additionally comprise further constituents, for example glycols, polyethylene glycols, polypropylene glycols, monoalkanolamides, undyed polymeric, inorganic or organic fillers, preservatives, UV filters or other adjuvants and additives conventionally employed in cosmetics.

25 Such further constituents are, for example, a natural or a synthetic or a semi-synthetic di- or tri-glyceride, a mineral oil, a silicone oil, a wax, a fatty alcohol, a Guerbet alcohol or an ester thereof, a lipophilic functional cosmetic active ingredient including sunscreens, or a mixture of such substances.

30 A lipophilic functional cosmetic active ingredient suitable for skin cosmetics, an active ingredient combination or an active ingredient extract is an ingredient or a mixture of ingredients that is approved for dermal or topical application. The following may be mentioned by way of example:

- 13 -

- active ingredients having a cleansing action on the skin surface and the hair. These include all substances that serve to cleanse the skin, such as oils, soaps, soapless detergents and solid substances;
- 5 - active ingredients having a deodorizing and perspiration-inhibiting action: they include antiperspirants based on aluminium or zinc salts, deodorants comprising bactericidal or bacteriostatic deodorizing substances, for example triclosan, hexachlorophene, alcohols and cationic substances, for example quaternary ammonium salts, and odour absorbers, for example ®Grillocin (combination of zinc ricinoleate and various additives) or triethyl citrate, optionally in combination with an antioxidant, for example butyl hydroxytoluene)
10 or ion-exchange resins;
- active ingredients that offer protection against sunlight (UV filters): suitable active ingredients are filter substances (sunscreens) that are able to absorb UV radiation from sunlight and convert it into heat. According to the desired action, the following light-protection agents are preferred: light-protection agents that selectively absorb sunburn-
15 causing high-energy UV radiation in the range of approximately from 280 to 315 nm (UV-B absorbers) and transmit the longer-wave range of approximately from 315 to 400 nm (UV-A range), as well as light-protection agents that absorb only the longer-wave radiation of the UV-A range of from 315 to 400 nm (UV-A absorbers).

Suitable light-protection agents are, for example, organic UV absorbers from the class of
20 the p-aminobenzoic acid derivatives, salicylic acid derivatives, benzophenone derivatives, dibenzoylmethane derivatives, diphenyl acrylate derivatives, benzofuran derivatives, polymeric UV absorbers comprising one or more organosilicon radicals, cinnamic acid derivatives, camphor derivatives, trianilino-s-triazine derivatives, phenylbenzimidazole sulfonic acid and salts thereof, menthyl anthranilates,
25 benzotriazole derivatives, and/or an inorganic micropigment selected from aluminium oxide- or silicon dioxide-coated TiO₂, zinc oxide or mica;
- active ingredients against insects (repellents): repellents are agents that are to prevent insects from touching the skin and becoming active there. They drive insects away and evaporate slowly. The most frequently used repellent is diethyl toluamide (DEET). Other
30 common repellents will be found in "W. Raab and U. Kindl, "Pflegekosmetik", Gustav-Fischer-Verlag Stuttgart/New York, 1991, p. 161;
- active ingredients providing protection against chemical and mechanical influences: these include all substances that form a barrier between the skin and external harmful

- substances, for example paraffin oils, silicone oils, vegetable oils, PCL products and lanolin for protection against aqueous solutions, film-forming agents, such as sodium alginate, triethanolamine alginate, polyacrylates, polyvinyl alcohol or cellulose ethers against the effect of organic solvents, or substances based on mineral oils, vegetable oils or silicone oils as "lubricants" against severe mechanical stresses on the skin;
- 5
- moisturizing substances: the following substances, for example, are used as moisture-controlling agents (moisturizers): sodium lactate, urea, alcohols, sorbitol, glycerol, propylene glycol, collagen, elastin or hyaluronic acid;
 - active ingredients having a keratoplastic effect: benzoyl peroxide, retinoic acid, colloidal sulfur and resorcinol;
 - 10
 - antimicrobial agents, for example triclosan or quaternary ammonium compounds;
 - oily or oil-soluble vitamins or vitamin derivatives that can be applied dermally: for example vitamin A (retinol in the form of the free acid or derivatives thereof), panthenol, pantothenic acid, folic acid, and combinations thereof, vitamin E (tocopherol), F;
 - 15
 - essential fatty acids; or niacinamide (nicotinic acid amide);
 - vitamin-based placenta extracts: active ingredient compositions comprising especially vitamins A, C, E, B₂₁, B₁₂, folic acid and biotin, amino acids and enzymes as well as compounds of the trace elements magnesium, silicon, phosphorus, calcium, manganese, iron or copper;
 - 20
 - skin repair complexes: obtainable from inactivated and disintegrated cultures of bacteria of the bifidus group;
 - plants and plant extracts: for example arnica, aloe, beard lichen, ivy, stinging nettle, ginseng, henna, camomile, marigold, rosemary, sage, horsetail or thyme;
 - animal extracts: for example royal jelly, propolis, proteins or thymus extracts;
 - 25
 - cosmetic oils that can be applied dermally: neutral oils of the Miglyol 812 type, apricot kernel oil, avocado oil, babassu oil, cottonseed oil, borage oil, thistle oil, groundnut oil, gamma-oryzanol, rosehip-seed oil, hemp oil, hazelnut oil, blackcurrant-seed oil, jojoba oil, cherry-stone oil, salmon oil, linseed oil, comseed oil, macadamia nut oil, almond oil, evening primrose oil, mink oil, olive oil, pecan nut oil, peach kernel oil, pistachio nut oil,
 - 30
 - rape oil, rice-seed oil, castor oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea tree oil, grapeseed oil or wheatgerm oil.

The preparations in stick form are preferably anhydrous but may in certain cases comprise a certain amount of water which, however, in general does not exceed 40 % by weight, based on the total weight of the cosmetic preparation.

If the cosmetic preparations and formulations according to the invention are in the form of semi-solid products, that is to say in the form of ointments or creams, they may likewise be anhydrous or aqueous. Such preparations and formulations are, for example, mascaras, eyeliners, foundations, make-up for the cheeks, eyeshadows, or compositions for treating rings under the eyes.

If, on the other hand, such ointments or creams are aqueous, they are especially emulsions of the water-in-oil type or of the oil-in-water type that comprise, apart from the pigment, from 1 to 98.8 % by weight of the fatty phase, from 1 to 98.8 % by weight of the aqueous phase and from 0.2 to 30 % by weight of an emulsifier.

Such ointments and creams may also comprise further conventional additives, for example perfumes, antioxidants, preservatives, gel-forming agents, UV filters, colourants, pigments, pearlescent agents, undyed polymers as well as inorganic or organic fillers.

If the preparations are in the form of a powder, they consist essentially of a mineral or inorganic or organic filler, for example, talc, zinc stearate, mica, kaolin, nylon powders (in particular Orgasol), polyethylene powders, Teflon, starch, boron nitride, microspheres of copolymers, such as Expancel (Nobel Industrie), Polytrap (Dow Corning), silicone resin microbeads (Tospearl from Toshiba, for example), polyethylene powder or polyamide powder, as well as adjuvants such as binders, colourants, etc..

The fillers may be present in an amount ranging from 0 to 35% of the total weight of the composition, preferably from 0.5 to 15%.

Such preparations may likewise comprise various adjuvants conventionally employed in cosmetics, such as perfumes, antioxidants, preservatives, etc..

If the cosmetic preparations and formulations according to the invention are nail varnishes, they consist essentially of nitrocellulose and a natural or synthetic polymer in the form of a solution in a solvent system, it being possible for the solution to comprise other adjuvants, for example pearlescent agents.

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In that embodiment, the dyed polymer is present in an amount of approximately from 0.1 to 5 % by weight.

The cosmetic preparations and formulations according to the invention may also be used for colouring the hair, in which case they are used in the form of shampoos, creams or gels that are composed of the basic substances conventionally employed in the cosmetics industry and comprise at least one pigment of formula as defined above.

The cosmetic preparations and formulations according to the invention are prepared in the conventional manner, for example by mixing or stirring the components together, optionally with heating, so that the mixtures melt.

The composition examples below are given by way of illustration and without a limiting nature.

The Examples which follow serve to illustrate the invention without limiting it thereto. Parts are parts by weight and percentages are percentages by weight. Temperatures are given in degrees Celsius.

The pigments of formula (Ia) as defined in Table 1 are used for the following formulation examples.

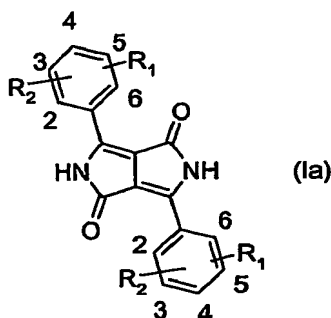


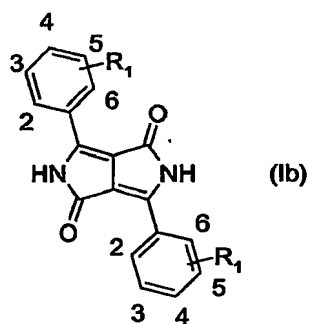
Table 1

Pigment	R ₁	R ₂
1	(3)-Cl	(4)-CH ₃
2	(3)-OCH ₃	(4)-OCH ₃
3	(3)-Cl	(4)-OC(CH ₃) ₂ CH ₂ CH ₃
4	(3)-CH ₃	(4)-CH ₃
5	(3)-Cl	(5)-Cl
6	(4)-Cl	(5)-Cl

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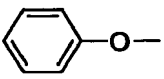
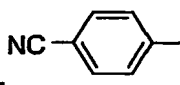
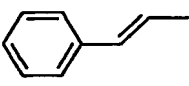
Pigment	R ₁	R ₂
7	(3)-OCH ₃	(5)-OCH ₃
8	(3)-CH ₃	(4)-Br

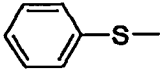
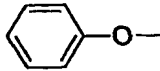

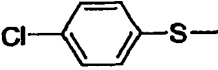
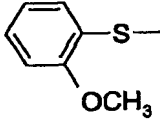
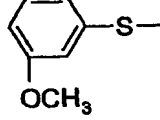
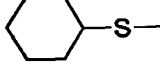
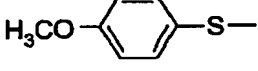
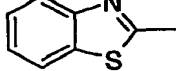
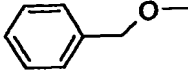
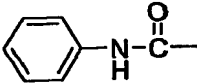
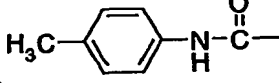
Further, the pigments of formula (Ib) as defined in Table 2 are used for the following formulation examples.

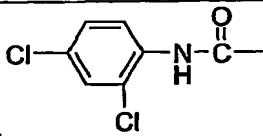
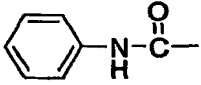
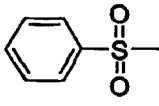
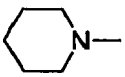
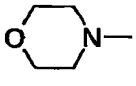
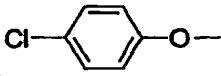
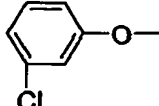
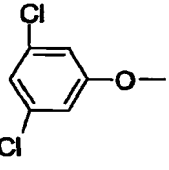
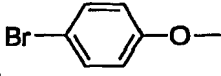
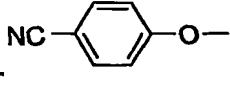
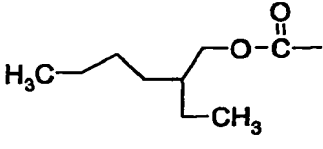


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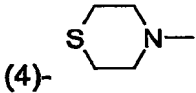
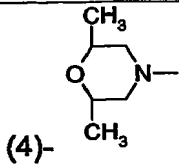
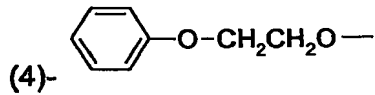
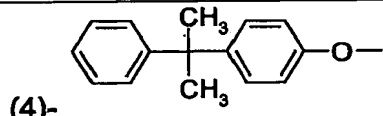
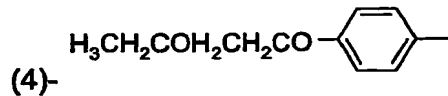
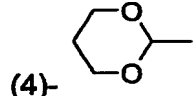
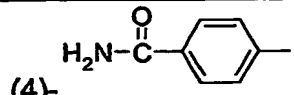
Table 2

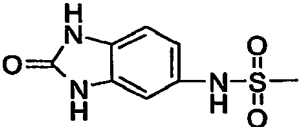
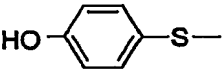
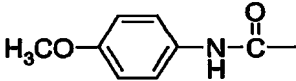
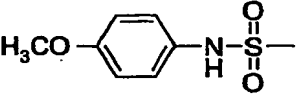
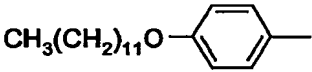
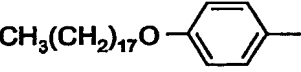
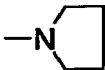
Pigment	R ₁
9	(4)-OCOCH ₃
10	(4)-SO ₂ CH ₃
11	(4)-CONH ₂
12	(3)-CONH ₂
13	(4)-N(CH ₃) ₂
14	(4)-CN
15	(3)-CF ₃
16	(4)-CF ₃
17	(3)- 
18	(3)-CN
19	(3)- 
20	(4)- 
21	(4)-SCH ₃

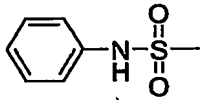
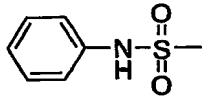
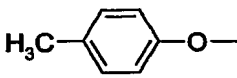
Pigment	R ₁
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23	(4)- 
24	(4)- 
25	(4)- 
26	(4)- 
27	(4)- 
28	(4)- 
29	(4)- 
30	(4)- 
31	(4)- 
32	(4)-SCH ₂ CH ₂ CH ₃
33	(3)- 
34	(4)- 

Pigment	R ₁
35	 (4)-
36	(4)-S(CH ₂) ₁₁ CH ₃
37	 (4)-
38	 (4)-
39	 (4)-
40	 (4)-
41	 (4)-
42	 (4)-
43	 (4)-
44	 (4)-
45	 (4)-
46	 (4)-
47	(4)-COOH

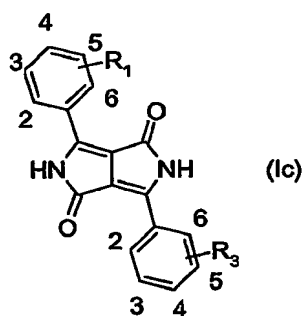
- 20 -

Pigment	R ₁
48	 (4)-
49	(4)-COOCH ₃
50	 (4)-
51	(4)-OH
52	(4)-COO(CH ₂) ₁₇ CH ₃
53	(3)-SO ₂ N(CH ₃) ₂
54	(3)-SO ₂ NH ₂
55	(4)-O(CH ₂) ₁₁ CH ₃
56	(4)-O(CH ₂) ₁₇ CH ₃
57	(4)-SO ₂ NH(CH ₂) ₃ CH ₃
58	 (4)-
59	 (4)-
60	(4)-C(CH ₃) ₃
61	(4)-(CH ₂) ₇ CH ₃
62	(4)-COOC(CH ₃) ₃
63	(4)-(CH ₂) ₃ CH ₃
64	(4)-OCF ₃
65	(4)-CON(CH ₂) ₁₇ CH ₃
66	 (4)-
67	 (4)-
68	 (4)-

Pigment	R ₁
69	 (4)-
70	(4)-COOCH ₂ C(CH ₃) ₃
71	(3)-CON(CH ₂ CH ₂ CH ₂ CH ₃) ₂
72	(4)-CONHCH ₃
73	(4)-CON(CH ₂ CH ₂ CH ₂ CH ₃) ₂
74	(4)-CH=CHCOO(CH ₂) ₃ CH ₃
75	(4)-S(CH ₂) ₁₇ CH ₃
76	 (4)-
77	 (4)-
78	(4)-O(CH ₂) ₂ OCH ₂ CH ₃
79	(4)-O(CH ₂) ₂ O(CH ₂) ₂ OCH ₂ CH ₃
80	(4)-S(CH ₂) ₂ N(CH ₃) ₂
81	 (4)-
82	 (4)-
83	(4)-O(CH ₂) ₅ CH ₃
84	(4)-S(CH ₂) ₅ CH ₃
85	(4)-O(CH ₂) ₂ CH ₃
86	 (4)-
87	(3)-O(CH ₂) ₂ CH ₃
88	 (4)-

Pigment	R ₁
89	
90	
91	

The pigments of formula (Ic) as defined in Table 3 are used for the following formulation examples.



5

Table 3

Pigment	R ₁	R ₃
92	(3)-CN	(4)-CN
93	(4)-COOCH ₃	H
94	(3)-CF ₃	(4)-Cl

All the above mentioned pigments are prepared according to known methods, whereby the specific surface is controlled by a proper selection of the method and the corresponding setup or reaction parameters of the given method by which the specific surface area could be achieved. Possible methods include for example grinding the crude pigments in the presence or absence of a solvent and where appropriate with the aid of grinding elements. Typical examples of grinding methods well known in the literature are dry grinding, wet grinding and kneading. The crude pigments can also be dissolved and re-precipitated from a solution in an appropriate solvent. Typical examples of solvents are concentrated sulphuric acid (acid pasting) or highly polar solvents with the addition of a small amount of a strong alkali. The

10

15

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solution of the colorant is then precipitated by mixing with water or an appropriate solvent with or without an acid or a base. Where appropriate, a pigment can also be grown to the desired surface area by stirring in a solvent or in an emulsion at a certain temperature (conditioning, Ostwald ripening). In certain cases, the desired surface area can also be achieved by a proper selection of the reaction conditions in the pigment synthesis and the subsequent hydrolysis/work up of the pigment. Generally, methods can also be combined to achieve the desired surface area. Milling and conditioning are also highly specific and have to be selected and developed depending on the individual pigment. References are given for example in WO 03/064541 and WO 02/068541.

Example: 1: Cheek Color

Number	Ingredients	Amount [%]
1	Sericite PHN	58.67
2	Zinc Stearate	4.55
3	Magnesium Carbonate NF Light	2.00
4	Boron Nitride	5.50
5	Methyl Paraben	0.20
6	Red Iron Oxide	2.44
7	Pigment 1	1.85
8	D&C Red 30 (Talc Blend)	3.76
9	Yellow Iron Oxide	1.36
10	Octyl Palmitate	5.00
11	Colorona Russet	8.73
12	Timica Sparkle	4.77
13	Duochrome RY	1.17

Ingredients 1 – 9 are added and mixed uniformly.

Ingredient 10 is sprayed into the phase and mixed until the phase is completely wetted out and uniform.

Ingredients 11 - 13 are added and the composition is mixed until uniform. Afterwards the mixture is passed through a micropulverizer.

A red cheek color having excellent in-use properties is obtained in that manner.

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Example 2: Cheek Color

Number	Ingredients	Amount [%]
1	Alpine Talc 141	60.80
2	Zinc Stearate	5.00
3	Kaolin	2.00
4	Boron Nitride	5.00
5	Methyl Paraben	0.20
6	Pigment 1	2.21
7	FD&C Yellow 5 Aluminum	0.57
8	Ultramarine Violet	1.46
9	Manganese Violet	3.73
10	Octyl Palmitate	5.00
11	Cloisonne Gold	7.75
12	Cloisonne Red	4.48
13	Flamenco Superpearl 100	1.80

Ingredients 1 – 9 are added and mixed uniformly. Ingredient 10 is sprayed into the phase and mixed until the phase is completely wetted out and uniform. Ingredients 11 and 12 are added and the composition is mixed until uniform. Afterwards the mixture is passed through a micropulverizer.

A red cheek color having excellent in-use properties is obtained in that manner.

Example 3: Powder Eyeshadow

Number	Ingredients	Amount [%]
1	Alpine Talc 141	57.58
2	Zinc Stearate	5.26
3	Boron Nitride	5.26
4	Propyl Paraben	0.32
5	Sericite PHN	10.53
6	Pigment 1	2.63
7	Ferric Ferrocyanide	0.53
8	Octyl Palmitate	5.26
9	Duochrome BR	12.63

Ingredients 1 – 7 are added and mixed uniformly. Ingredient 8 is sprayed into the phase and mixed until the phase is completely wetted out and uniform. Ingredient 9 is added and the

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composition is mixed until uniform. Afterwards the mixture is passed through a micropulverizer.

Powder eyeshadow having excellent in-use properties is obtained in that manner.

5 **Example 4: Eyeshadow Formulation**

Number	Ingredients	Amount [%]
1	Sericite PHN	57.59
2	Zinc Stearate	5.26
3	Boron Nitride	5.26
4	Propyl Paraben	0.32
5	Wet Ground Mica PGM-3	5.26
6	Nylon-12	5.26
7	Pigment 1	2.63
8	Ferric Ferrocyanide	0.53
9	Octyl Palmitate	5.26
10	Duochrome BR	12.63

The formulation is prepared in analogy of Example 3.

A powder eyeshadow having excellent in-use properties is obtained in that manner.

10 **Example 5: A waterproof eyeshadow cream having excellent in-use properties has the following composition:**

Number	Ingredients	Amount [%]
1	acrylic acid/butyl acrylate/methyl methacrylate copolymer, 30 % emulsion	10.00
2	Pigment 1	10.00
3	mineral oil	8.50
4	glycerol	5.50
5	microcrystalline wax	3.00
6	stearic acid	3.00
7	ultramarine blue	2.00
8	sorbitan monostearate	1.50
9	TEA	1.50
10	lanolin	1.00

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Number	Ingredients	Amount [%]
11	methyl-hydroxypropylcellulose	0.50
12	preservative	qs
13	water	to 100

Example 6: A waterproof eyeshadow gel having excellent in-use properties has the following composition:

Number	Ingredients	Amount [%]
1	propylene glycol	5.00
2	sucrose distearate	3.00
3	isopropyl palmitate	3.00
4	mineral oil	3.00
5	lanolin oil	2.00
6	synthetic hectorite	2.00
7	di-Na-EDTA	0.02
8	Pigment 1	1.00
9	CI Pigment Blue 15	0.50
10	preservative	qs
11	water	to 100

5 Example 7: Face powder

Number	Ingredients	Amount [%]
1	Alpine Talc 141	33.97
2	Wet Ground Mica PGM-3	5.00
3	Zinc Stearate	5.00
4	Nylon-12	3.00
5	Aluminum Starch Octenylsuccinate	25.00
6	Boron Nitride	2.00
7	Silica	10.00
8	Methyl Paraben	0.25
9	Propyl Paraben	0.10
10	Imidazolidinyl Urea	0.30
11	Magnesium Carbonate NF Light	1.00
12	TiO ₂ pigment	6.00

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Number	Ingredients	Amount [%]
13	Pigment 1	0.08
14	Yellow Iron Oxide	1.10
15	Black Iron Oxide	0.10
16	Octyl Palmitate	3.00
17	Lanolin Oil	3.00
18	Tocopheryl Acetate	0.10
19	Mineral Oil	1.00

Ingredients 1 – 15 are added and mixed uniformly. The mixture is passed through a micropulverizer. After mixing, ingredients 16 – 19 are sprayed into the phase and mixed until the phase is completely wetted out and uniform. Afterwards the mixture is passed through a

5

micropulverizer.
A face powder having excellent in-use properties is obtained in that manner.

Example 8: Powder Foundation

Number	Ingredients	Amount [%]
1	Alpine Talc 141	50.3
2	Sericite PHN	21.71
3	Zinc Stearate	6.12
4	Kaolin	1.02
5	Silica	1.02
6	Boron Nitride	3.32
7	Methyl Paraben	0.31
8	Magnesium Carbonate NF Light	1.53
9	Pigment 1	1.08
10	Black Iron Oxide	0.56
11	Yellow Iron Oxide	7.03
12	TiO ₂ pigment	0.90
13	Octyl Palmitate	4.08
14	Lanolin Alcohol	1.02

10 Ingredients 1 – 12 are added and mixed uniformly. The mixture is passed through a micropulverizer. After mixing at elevated temperature, ingredients 13 and 14 are sprayed into the phase and mixed until the phase is completely wetted out and uniform. Afterwards the mixture is passed through a micropulverizer.

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A powder foundation having excellent in-use properties is obtained in that manner.

Example 9: Face Powder

Number	Ingredients	Amount [%]
1	Alpine Talc 141	75.8
2	Sericite PHN	9.62
3	Zinc Stearate	5.15
4	Magnesium Carbonate NF Light	0.10
5	Nylon-12	1.01
6	Silica	1.01
7	Pigment 1	0.84
8	Yellow Iron Oxide	2.53
9	Black Iron Oxide	0.51
10	Methyl Paraben	0.20
11	Propyl Paraben	0.10
12	Octyl Palmitate	1.01
13	Mineral Oil	1.01
14	Dimethicone	1.01
15	Tocopheryl Acetate	0.10

- 5 Ingredients 1 – 11 are added and mixed uniformly. The mixture is passed through a micropulverizer. After mixing, ingredients 12 – 15 are sprayed into the phase and mixed until the phase is completely wetted out and uniform. Afterwards the mixture is passed through a micropulverizer.

A face powder having excellent in-use properties is obtained in that manner.

10

Example 10: A foundation of the following composition is used:

Number	Ingredients	Amount [%]
1	Cutina KD 16	0.80
2	Cutina FS 45	1.40
3	Lanette 16	1.00
4	Arlacel 60	0.20
5	paraffin oil pearl	8.00
6	isopropyl stearate	6.00
7	Myritol 318	4.00

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Number	Ingredients	Amount [%]
8	Softisan 100	2.00
9	Abil 100	0.20
10	Controx KS	0.05
11	Uniphen P 23	1.00
12	talcum Pharma G	5.00
13	titanium white	6.00
14	Pigment 1	1.50
15	demineralized H ₂ O	56.10
16	propylene carbonate	0.10
17	Veegum ultra	0.80
18	glycerol 87 %	5.00
19	Natrosol 250 HHR	0.30
20	TEA C, pure	0.55

Substances 1 - 11 are melted together, and substance 12 is dispersed in that mixture. The mixture is then heated to from 75 to 80°C.

Separately therefrom, substances 15 and 16 are mixed, and substance 17 is dispersed
5 homogeneously in that mixture. Substance 19 is then distributed homogeneously in that mixture; once the increase in swelling has ceased, substance 18 is stirred in and the whole mixture is heated to from 75 to 80°C.

The second mixture is then added to the first mixture, with intensive stirring, substance 20 is then stirred in homogeneously, and the resulting emulsion is stirred until it has cooled to
10 room temperature. Substances 13 and 14 are then dispersed in by means of a dissolver, and the resulting make-up is then passed through a triple roller.

There is obtained a red make-up having excellent in-use properties and an intense bright red colour of outstanding fastness to light.

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Example 11: A powder foundation of the following composition is used

Number	Ingredients	Amount [%]
Phase A		
1	Talc	48.20
2	Mica and Methicone (Toshiki Sericite OS-61D)	34.00
3	Pigment 1	5.00
4	Kaolin	6.00
5	Zinc Stearate	3.00
6	Methyl Paraben	0.20
7	Propyl Paraben	0.10
Phase B		
8	Dicaprylyl Maleate	3.00
9	PEG-400 Diisostearate	0.50

Phase A is put into high shear mixer and mixed until color are completely extended. All ingredients of phase B are put together and mixed until phase B is fully homogenous.

5 Phase B is sprayed to phase A with high mixing.

The united phases are mixed fully homogenous by a high shear mixer.

There is obtained a powder foundation having excellent in-use properties and an intense bright red colour of outstanding fastness to light.

10 **Example 12:** Lipstick Formulation

Number	Ingredients	Amount [%]
1	Castor Oil LISP	15.00
2	Pigment 1	1.40
3	FD&C Blue 1 B3016 Aluminum Lake	0.25
4	FD&C Yellow 5 B3014 Aluminum Lake	0.20
5	TiO ₂ pigment	3.00
6	Cosmetic Yellow C33-8073	1.00
7	Red Iron Oxide 3080	3.20
8	Castor Oil LISP	31.40
9	White Beeswax	2.00

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Number	Ingredients	Amount [%]
10	Permalene 400	4.00
11	Camauba Wax	2.00
12	Candelilla Wax	5.00
13	Caprylic/Capric Triglyceride	8.00
14	Octyl Methoxycinnamate	7.50
15	Lanolin Oil	2.00
16	Stearyl Alcohol	2.00
17	Jobba Oil	6.00
18	Shea Butter	2.00
19	Cetyl Palmitate	3.00
20	Propyl Paraben	0.20
21	Tocopheryl Acetate	0.10
22	Lipstick Fragrance	0.75

Ingredients 8 – 21 are mixed at a temperature of 75 – 80°C until the phase is uniform. Ingredients 1 - 7 are mixed together and grinded in a ball mill or 3-roll mill. Afterwards ingredients 1 – 7 are added to the mixture of ingredients 8 – 21. The mixture is mixed at a temperature of 75 – 80°C. Afterwards Ingredient 22 is added and the mixture is mixed at a temperature of about 70°C.

A lipstick having excellent in-use properties is obtained in that manner.

Example 13: Lipstick Formulation

Number	Ingredients	Amount [%]
1	Ozokerite Wax	4.02
2	Camauba Wax	3.76
3	Candelilla Wax	4.74
4	White Beeswax	7.98
5	Myristyl Lactate	5.37
6	Octyl Palmitate	3.63
7	Shea Butter	1.00
8	Isopropyl Palmitate	3.45
9	Castor Oil USP	41.62
10	Propyl Paraben	0.20
11	Isopropyl Isostearate	2.55
12	Castor Oil USP	10.00

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Number	Ingredients	Amount [%]
13	Pigment 1	2.74
14	TiO ₂ pigment	3.22
15	Red Iron Oxide 3080	1.23
16	FD&C Yellow 5 B3014 Aluminum Lake	1.78
17	FD&C Blue 1 B3016 Aluminum Lake	0.21
18	Cloisonne Gold	2.00
19	Lipstick Fragrance	0.50

Ingredients 1 – 11 are mixed at a temperature of 75 – 80°C until the phase is uniform. Ingredients 12 - 18 are mixed together and grinded in a ball mill or 3-roll mill. Afterwards ingredients 12 – 18 are added to the mixture of ingredients 1 – 11. The mixture is mixed at a temperature of 75 – 80°C. Afterwards Ingredient 19 is added and the mixture is mixed at a temperature of about 70°C.

A lipstick having excellent in-use properties is obtained in that manner.

Example 14: A lipstick base of the following composition is used:

Number	Ingredients	Amount [%]
1	cera alba	11.40
2	candelilla wax	8.10
3	carnauba wax	3.80
4	Lunacera M	6.00
5	castor oil	38.80
6	Controx KS	0.10
7	aromatic oil	1.00
8	Amerlate P	2.50
9	OH lan	1.60
10	isopropyl palmitate	10.10
11	Dow Corning 556	2.80
12	Dow Corning 1401	3.30
13	TiO ₂ pigment	2.30
14	Pigment 1	8.20

Substances 8 - 10 are mixed together, and substances 13 and 14 are dispersed in that mixture. The resulting paste is then passed several times through a triple roller.

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In the meantime, substances 1 - 6 are melted and stirred together homogeneously, and then substances 7, 11 and 12 are stirred in.

The two mixtures are then mixed together while hot until homogeneous distribution is achieved. The hot mass is then poured into a lipstick mould and allowed to cool.

- 5 There are obtained lipsticks having an intense bright red colour of outstanding fastness to light and very good gloss.

Example 15: A water-in-oil lipstick emulsion having the following composition is prepared analogously to Example 14:

Number	Ingredients	Amount [%]
1	mineral oil	28.50
2	glycerol bis(2-heptylundecanoate)	28.50
3	Pigment 1	9.20
4	polyethylene wax	10.00
5	candelilla wax	10.00
6	ceresin wax	5.7
7	water	3.00
8	glycerol	2.00
9	carnauba wax	1.40
10	castor oil	1.45
11	magnesium aluminium silicate	0.15
12	benzyltrimethylstearyl ammonium chloride	0.05
13	hydrogenated lecithin	0.05

10

There are obtained lipsticks having an intense bright red colour of outstanding fastness to light and very good gloss.

Example 16: An oil-in-water lipstick emulsion having the following composition is prepared analogously to Example 14:

15

Number	Ingredients	Amount [%]
1	glycerol tri-2-ethylhexanoate	31.80
2	jojoba oil	20.00
3	ceresin wax	10.00
4	castor oil	10.00

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Number	Ingredients	Amount [%]
5	Pigment 1	10.00
6	lanolin oil	5.00
7	water	5.00
8	microcrystalline wax	3.00
9	carnauba wax	2.00
10	surface-active substances based on alkyl ethers	2.00
11	glycerol	1.00
12	polyvinyl alcohol	0.20

There are obtained lipsticks having an intense bright red colour of outstanding fastness to light and very good gloss.

- 5 Example 17: A non-greasy lipstick having the following composition is prepared analogously to Example 14:

Number	Ingredients	Amount [%]
1	white beeswax	20.00
2	ozocerite	10.00
3	Pigment 1	9.00
4	anhydrous lanolin	5.00
5	propylene glycol recinoleate	4.00
6	liquid paraffin	3.00
7	isopropyl myristate	3.00
8	carnauba wax	2.50
9	cetyl alcohol	2.00
10	CI Pigment Blue 15	1.00
11	castor oil	40.50

There are obtained lipsticks having an intense bright red colour of outstanding fastness to light and very good gloss.

Example 18: A transfer-resistant lipstick having the following composition is prepared analogously to Example 14:

Number	Ingredients	Amount [%]
1	cyclomethicone	50.00
2	isodecane	12.00
3	Pigment 1	8.00
4	synthetic wax	7.20
5	isostearyltrimethylpropane-siloxy silicate	6.00
6	cetyl stearate/acetylated lanolin, 90:10	6.00
7	ceresin	4.80
8	paraffin	3.60
9	TiO ₂ pigment	2.00
10	methylparaben	0.30
11	propylparaben	0.10

There are obtained lipsticks having an intense bright red colour of outstanding fastness to
5 light and very good gloss.

Example 19: Liquid Make-up Formulation

Number	Ingredients	Amount [%]
1	Deionized Water	50.46
2	Magnesium Aluminum Silicate	2.06
3	Carboxy Methyl Cellulose	0.1
4	Lecithin	0.10
5	Methyl Paraben	0.31
6	Imidazolidinyl Urea	0.52
7	Butylene Glycol	5.16
8	Triethanolamine 99%	2.06
9	Kaolin	2.06
10	TiO ₂ pigment	7.73
11	Yellow Iron Oxide	5.46
12	Pigment 1	1.55
13	Black Iron Oxide	0.46
14	Alpine Talc 141	2.06
15	Stearic Acid	6.19

Number	Ingredients	Amount [%]
16	Glyceryl Monostearate Pure	2.58
17	Isopropyl Lanolate	2.06
18	Lanolin Alcohol	0.21
19	Mineral Oil	8.25
20	Propyl Paraben	0.10
21	Makeup Fragrance	0.52

Ingredients 1 – 4 are mixed and the ingredients 5 – 14 are added to the phase and the composition is mixed until completely uniform. The mixture is milled using either a colloid mill or ball mill. This composition is mixed at a temperature of about 75°C.

- 5 Ingredients 15 – 20 are mixed and heated up to 75°C. Afterwards the oil phase is slowly added to the water phase with continuous mixing. After cooling to 50°C ingredient 21 is added and the composition is mixed until completely uniform.

A liquid make-up formulation having excellent in-use properties is obtained in that manner.

10 **Example 20: Make-up Formulation**

Number	Ingredients	Amount [%]
1	Deionized Water	61.21
2	Butylene Glycol	8.00
3	Xanthan Gum	0.34
4	Magnesium Aluminum Silicate	0.51
5	Imidazolidinyl Urea	0.25
6	Methyl Paraben	0.30
7	Triethanolamine 99%	1.31
8	Silica	2.50
9	TiO ₂ pigment	5.10
10	Pigment 1	0.15
11	Yellow Iron Oxide	0.90
12	Black Iron Oxide	0.05
13	Cetyl Ethylhexanoate	3.54
14	Decyl Oleate	3.54
15	C ₁₂₋₁₅ Alkyl Benzoate	2.53
16	Stearic Acid	3.54
17	Isostearic Acid	1.01
18	Cetyl Alcohol	0.51

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Number	Ingredients	Amount [%]
19	Caprylic/Capric Triglyceride	1.01
20	Propyl Paraben	0.15
21	BHT	0.05
22	Dimethicone	3.50

Ingredients 1 – 4 are mixed and the ingredients 5 – 12 are added to the phase and the composition is mixed until completely uniform. The mixture is milled using either a colloid mill or ball mill. This composition is mixed at a temperature of about 75°C.

- 5 Ingredients 13 – 22 are mixed and heated up to 75°C. Afterwards the oil phase is slowly added to the water phase with continuous mixing.

A make-up formulation having excellent in-use properties is obtained in that manner.

Example 21: A make-up stick having excellent in-use properties has the following

- 10 composition:

Number	Ingredients	Amount [%]
1	mineral oil and lanolin alcohol	22.50
2	Laneth-5	15.00
3	TiO ₂ pigment	11.00
4	cetyl alcohol	5.00
5	carnauba wax	4.50
6	Pigment 1	4.00
7	yellow iron oxide	4.00
8	candilla wax	0.50
9	perfume and preservative	qs
10	oleyl alcohol	to 100

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Example 22: A blusher (powder) having excellent in-use properties has the following composition:

Number	Ingredients	Amount [%]
1	talcum	58.00
2	zinc stearate	15.00
3	rice starch	15.00
4	Pigment 1	12.00
5	perfume	q.s.

Example 23: The following substances are used for a nail varnish:

Number	Ingredients	Amount [%]
1	sodium selenite	0.01
2	ethyl acetate	20.00
3	isobutyl acetate	26.99
4	isopropyl alcohol	2.00
5	toluene	20.00
6	nitrocellulose	17.00
7	saccharose acetate isobutyrate	8.00
8	dibutyl phthalate	3.80
9	1,3-butylene glycol	0.20
10	Pigment 1	1.00
11	stearylalkonium hectorite	1.00

5

A red nail varnish having very good in-use properties and outstanding gloss is obtained. After application of the nail varnish, a waiting period of three days and removal of the nail varnish, it is found that the nail has remained completely unstained.

10

Example 24: The following substances are used for a water-based nail varnish:

Number	Ingredients	Amount [%]
1	demineralized water	58.85
2	TiO ₂ pigment	5.60
3	Pigment 1	2.16
4	talcum	5.72
5	potassium cetyl phosphate	1.50
6	propylene glycol	8.00
7	Mg-Al silicate	1.00
8	cellulose gum (high viscosity)	0.14
9	ester of saccharose and coconut fatty acid	0.20
10	methylparaben	0.20
11	EDTA	0.05
12	propylene glycol dicaprylate/dicaprate	10.80
13	isostearyl-stearyl stearate	2.00
14	sorbitan monolaurate	3.00
15	cetyl alcohol	0.50
16	propylparaben	0.10
17	DMDM-hydantoin	0.18

A red nail varnish having very good in-use properties and outstanding gloss is obtained. After application of the nail varnish, a waiting period of three days and removal of the nail varnish,

5 it is found that the nail has remained completely unstained.

Example 25: The following substances are used for a mascara formulation:

Number	Ingredients	Amount [%]
1	stearic acid	3.50
2	glycerol stearate	6.00
3	beeswax	7.00
4	propylparaben	0.10
5	demineralized water	38.25
6	methylparaben	0.10
7	polyvinylpyrrolidone	6.00

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Number	Ingredients	Amount [%]
8	propylene glycol	3.00
9	sodium carboxymethylcellulose	0.15
10	pigment 1	10.40
11	kaolin	3.50
12	ethyl acrylate/methyl acrylate (8/2)	22.00

Mixtures of substances 1 to 4 and 5 to 9 are heated separately from one another until homogeneous mixtures are formed; the mixtures are then combined and stirred thoroughly until a homogeneous phase is obtained. Components 10 and 11 are then dispersed in a portion of that phase, and the dispersion is then added to the remainder. Component 12 is then added with stirring.

A mascara formulation having excellent in-use properties is obtained in that manner.

Example 26: A mascara formulation for hair is prepared from the following components:

Number	Ingredients	Amount [%]
1	mascara base (mixture of beeswax, carnauba wax, stearic acid, Ceteareth 25, PEG-2 stearate, mineral oil, hydrogenated coconut oil and cetyl alcohol)	15.00
2	dimethicone	1.50
3	preservative	0.50
4	demineralized water	42.10
5	triethanolamine 85 %	0.45
6	thickener mixture (xanthan gum, hectorite, cellulose gum)	0.45
7	pigment 1	10.00
8	acrylate copolymer	30.00

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Ingredients 1 are heated to approximately 75°C, with slow stirring, in a steel tank. In a separate vessel, ingredient 3 is dissolved in ingredient 4, and ingredient 6 is added in such a manner as to obtain a gel that is homogeneous at room temperature. Ingredients 2 and 5 are then added, and heating to approximately 75°C is carried out. With moderate stirring, the mixture of ingredients 2, 3, 4, 5 and 6 is added to ingredient 1, and stirring is carried out until the product is homogeneous. Ingredient 7 is dispersed in a portion of that product by means of

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a three-roll mill, ingredient 8 is added with stirring, and the dispersion is then added to the remainder of the product and mixed thoroughly.

A mascara formulation for hair having good in-use properties is obtained.

- 5 **Example 27:** A water-in-oil mascara having excellent in-use properties has the following composition:

Number	Ingredients	Amount [%]
1	polyisobutylene	57.60
2	microcrystalline wax	20.00
3	Pigment 1	10.00
4	carnauba wax	7.00
5	bentonite	3.00
6	beeswax	2.00
7	lanolin	0.40

Example 28: A hair mascara having the following composition is prepared analogously to Example 26:

Number	Ingredients	Amount [%]
1	Pigment 1	12.00
2	white beeswax	6.50
3	propylene glycol	6.00
4	carnauba wax	4.25
5	cetearyl alcohol and dicetyl phosphate and ceteth-10 phosphate (Crodafos CES)	4.00
6	PVP/hydrolysed wheat protein copolymer	4.00
7	Steareth-10	1.00
8	stearyl alcohol	1.00
9	PVP	1.00
10	Steareth-2	0.50
11	Laneth-5	0.50
12	potassium hydroxide	0.24
13	hydroxyethylcellulose	0.10
14	di-Na-EDTA	0.10

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Number	Ingredients	Amount [%]
15	preservative	qs
16	water	to 100

A mascara formulation for hair having good in-use properties is obtained.

Example 29: A foundation cream having excellent in-use properties has the following composition:

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Number	Ingredients	Amount [%]
1	TiO ₂ pigment	12.79
2	oleyl alcohol	4.57
3	glycerol stearate	3.65
4	propylene glycol	3.65
5	stearic acid	1.83
6	magnesium aluminium silicate	0.91
7	triethanolamine 99 %	0.91
8	CI Iron Oxide Yellow	0.64
9	Pigment 1	0.42
10	CI Pigment Brown 6	0.37
11	carboxymethylcellulose	0.10
12	water	to 100

In every formulation Example 1 – 29, Pigment 1 can be replaced by any of the pigments 2 – 24, as well as by mixtures of pigments 1 – 24 as well as by mixtures of pigments 1 – 24 with one or more other suitable pigments as described above.

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